

Technology Information

Immobilization of heavy metals by directed and controlled BaSO₄ precipitation

1. FUNDAMENTALS

BaSO₄ has a solubility product of 10^{-10} mol²/l² and is a mineral which is stable in most naturally occurring solutions. Due to the extremely low solubility, even traces of Ba²⁺ ions are precipitated in the presence of SO₄²⁻ ions. Only the addition of special precipitation inhibitors offers the possibility of synthesizing solutions oversaturated in BaSO₄. These chemicals prevent spontaneous precipitation during the preparation of the solution (for example by mixing of BaCl₂ and MgSO₄ solutions) and stabilize the oversaturation for a limited period of time (Fig. 1). A favorable way to prepare "pure" BaSO₄ solutions is using Ba(OH)₂ solutions and diluted H₂SO₄. Apart from the inhibitor, the resulting solution contains only Ba²⁺ and SO₄²⁻ ions. The timely course of the precipitation process can be directed by the selection of the inhibitor composition and concentration (Fig. 2). The maximum achievable BaSO₄ supersaturation lies between 200 and 400 mg/l, depending on the type of inhibitor and its concentration. Decomposition of the inhibitor results in the formation of insoluble BaSO₄ precipitates.

Immobilization is achieved both by formation of slightly soluble precipitates and overlaying of reactive mineral surfaces by insoluble BaSO₄ (Fig. 3). Encapsulation of polluted areas by creation of low permeable zones is another possible way to fix contaminants in-situ.

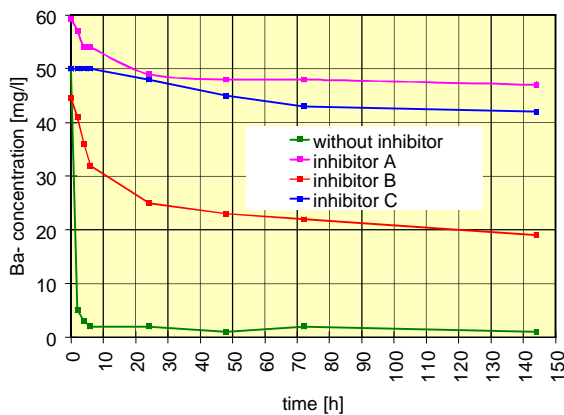


Fig. 1: Course of BaSO₄ precipitation depending on the used inhibitor

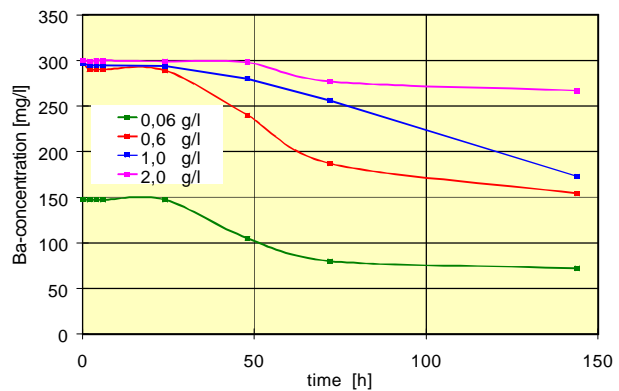


Fig. 2: Course of BaSO₄ precipitation depending on the inhibitor concentration

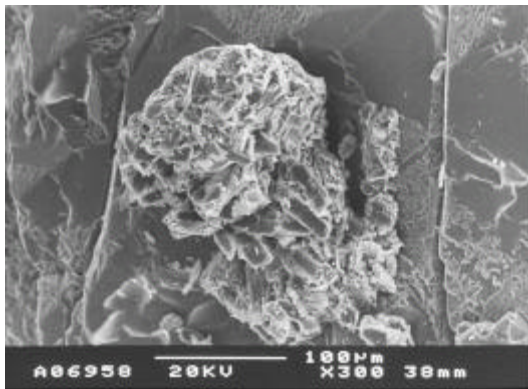


Fig. 3: SEM picture of BaSO₄ layers grown on sandstone particles

2. RESULTS OF TECHNICAL USE

The developed process was applied successfully in the former uranium mine Königstein of Wismut GmbH, Germany. In this mine uranium was recovered by in-situ leaching of a sandstone formation with diluted H₂SO₄. After the end of mining operations large amounts of acidic, contaminated solutions were present in the formation, which had to be treated before flooding the mine. Between 2003 and 2005 approximately 250,000 m³ BaSO₄ solution were injected in order to immobilize heavy metals.

The solution was pumped into the formation and after passing the formation the output was collected at a lower horizon (Fig. 4). During the injection of the BaSO₄ grout significant reduction in permeability was found (Fig. 5).

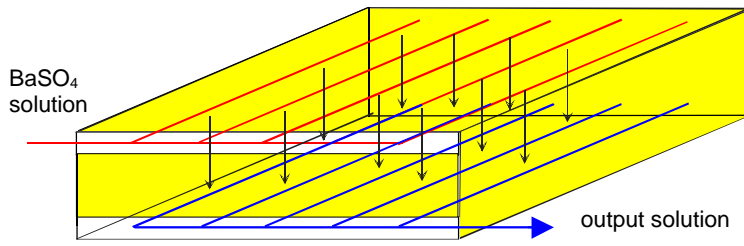


Fig. 4 Schematic view of the test site

The dimensions of this effect were surprising because the absolute amounts of BaSO₄ brought into the formation were low in relation to the pore volume. The composition of the solutions collected after passing the sandstone formation is summarized in Fig. 6.

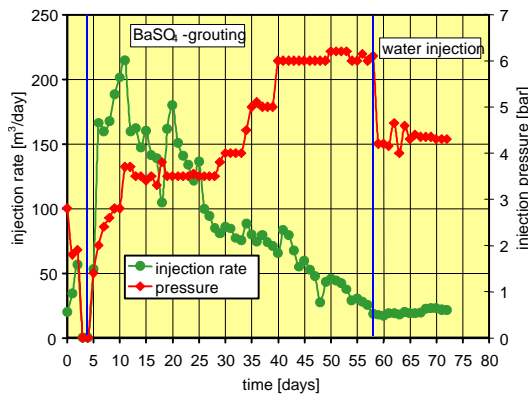


Fig. 5: Development of injection rate and pressure

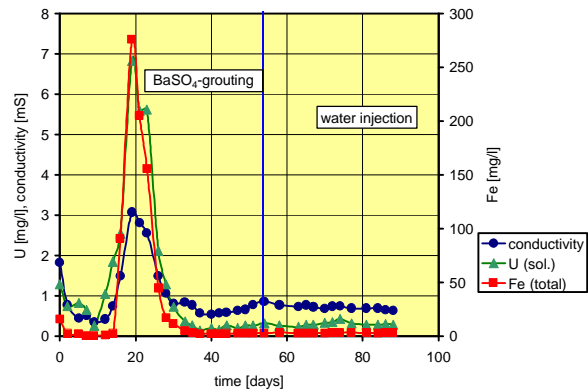


Fig. 6: Course of contaminants in the output solutions

In the first step the injected grout penetrated preferred flow paths with a high hydraulic conductivity and led to an immobilization of contaminants in these flow routes. With increasing amounts of injected BaSO₄ grout, zones with lower permeability were also reached and the maximum of the concentrations in the output solutions reflects pore water which is undiluted or only affected by low amounts of BaSO₄ grout. The penetration of zones with lower permeability was supported by a closure of bigger flow paths by newly formed BaSO₄ precipitates. Further concentration development was characterized by rapid decrease in the contents of all components. The BaSO₄ grout has led to in-situ precipitation processes and to the formation of protective layers. After finishing the BaSO₄ grouting, the test area was treated with fresh water for three weeks. No dissolution processes and no increase in the permeability of the formation took place. The output solution did not contain Ba²⁺ ions. The level of contaminants remained low.

3. CONCLUSION

The directed and controlled crystallization of BaSO₄ from oversaturated solutions is a favorable method to fix contaminants by precipitation. Reactive mineral surfaces can be protected against leaching by layers of insoluble minerals. The immobilization is connected with a drastic reduction of the hydraulic conductivity of the treated formation. It is not necessary to fill the flow paths with secondary minerals to obtain sealing. Even closure by single crystals leads to a drastic reduction in permeability.

The large scale application of BaSO₄-solutions has demonstrated that grouts supersaturated in slightly soluble minerals can be prepared in a simple way under conditions typical for the mining industry. The total costs of chemicals are low and immobilization and sealing is achieved by minerals naturally present in the rock or soil formation. The method has the essential benefits of mineral crystallization directly from the injection solution as well as multiple possibilities to control both the crystallization and immobilization process.